BOUND and FIELD: programs for calculating bound states of interacting pairs of atoms and molecules

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Abstract

The BOUND program calculates the bound states of a complex formed from two interacting particles using coupled-channel methods. It is particularly suitable for the bound states of atom-molecule and molecule-molecule van der Waals complexes and for the near-threshold bound states that are important in ultracold physics. It uses a basis set for all degrees of freedom except R, the separation of the centres of mass of the two particles. The Schrödinger equation is expressed as a set of coupled equations in R. Solutions of the coupled equations are propagated outwards from the classically forbidden region at short range and inwards from the classically forbidden region at long range, and matched at a point in the central region. Built-in coupling cases include atom + rigid linear molecule, atom + vibrating diatom, atom + rigid symmetric top, atom + asymmetric or spherical top, rigid diatom + rigid diatom, and rigid diatom + asymmetric top. Both programs provide an interface for plug-in routines to specify coupling cases (Hamiltonians and basis sets) that are not built in. With appropriate plug-in routines, BOUND can take account of the effects of external electric, magnetic and electromagnetic fields, locating bound-state energies at fixed values of the fields. The related program FIELD uses the same plug-in routines and locates values of the fields where bound states exist at a specified energy. As a special case, it can locate values of the external field where bound states cross scattering thresholds and produce zero-energy Feshbach resonances. Plug-in routines are supplied to handle the bound states of a pair of alkali-metal atoms with hyperfine structure in an applied magnetic field.

Keywords: bound states, ultracold, external fields, wavefunctions

PROGRAM SUMMARIES

Manuscript Title:
Authors: Jeremy M. Hutson and C. Ruth Le Sueur
Program Titles: BOUND and FIELD
Journal Reference:
Catalogue identifier:
Licensing provisions:
Programming language: Fortran 90
Computer:
Operating system:
RAM: case dependent
Keywords: bound states, ultracold, external fields, wavefunctions
Classification: 16.1 Structure and properties
External routines/libraries: LAPACK, BLAS
Subprograms used:
Nature of problem: Solve the Schrödinger equation to locate the bound states of an interacting pair of atoms or molecules as a function of energy (for BOUND) or external field (for FIELD).

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Solution method:
The Schrödinger equation is expressed in terms of coupled equations in the interparticle distance, R. Solutions of the coupled-channel equations are propagated outwards from the classically forbidden region at short range and inwards from the classically forbidden region at long range, and matched at a point in the central region. Bound states exist at energies where one of the eigenvalues of the log-derivative matching matrix is zero. BOUND calculates the number of bound states in a specified range of energy and then converges on the bound-state energies. FIELD operates in a similar manner to BOUND but converges on bound states as a function of external field at fixed energy, or energy fixed with respect to a field-dependent threshold energy. The programs can also generate bound-state wavefunctions if desired.

Restrictions:

Unusual features:

1. The programs include Hamiltonians for simple atom-molecule and molecule-molecule interactions, and provide an interface that allows users to specify Hamiltonians and basis sets for more complex systems. This interface allows users to include multiple external fields in the Hamiltonian.
2. The programs can propagate very efficiently to long range, making them particularly suited to locating very high-lying bound states.

Additional comments:

Running time: highly dependent on mass and complexity of interacting particles

1. Introduction

There are many different types of bound-state problem that arise in atomic and molecular physics. These range from the electronic structure problem, involving antisymmetrised many-particle wavefunctions and Coulomb interaction potentials, to low-amplitude molecular vibrational problems that can be solved in basis sets of harmonic-oscillator functions. In the absence of wide-amplitude motion, the rovibrational bound-state problem is often formulated in terms of Eckart-Watson Hamiltonians [1, 2, 3]. Wide-amplitude motion and exchange of identical nuclei often require special techniques, even when the motion takes place on a single electronic potential-energy surface [4, 5, 6, 7].

The BOUND and FIELD programs deal with an intermediate set of problems involving interactions between two particles (atoms or molecules), in some cases on multiple coupled surfaces, where the total Hamiltonian of the system may be written

$$H = -\frac{\hbar^2}{2\mu} R^{-1} \frac{d^2}{dR^2} R + \frac{\hbar^2 \hat{L}^2}{2\mu R^2} + H_{\rm intl}(\xi_{\rm intl}) + V(R, \xi_{\rm intl}), \tag{1}$$

where R is a radial coordinate describing the separation of two particles and $\xi_{\rm intl}$ represents all the other coordinates in the system. $H_{\rm intl}$ represents the sum of the internal Hamiltonians of the isolated particles, and depends on $\xi_{\rm intl}$ but not R, and $V(R, \xi_{\rm intl})$ is an interaction potential. The operator $\hbar^2 \hat{L}^2 / 2\mu R^2$ is the centrifugal term that describes the end-over-end rotational energy of the interacting pair.

The Hamiltonian (1) is usually appropriate for pairs of particles that interact weakly enough that the particles retain their chemical identity. Such problems commonly arise in the spectroscopy of van der Waals complexes [8] and in the near-threshold bound states that are important in the creation and control of ultracold molecules [9]. The internal Hamiltonian $H_{\rm intl}$ is a sum of terms for the two particles 1 and 2,

$$H_{\rm intl}(\xi_{\rm intl}) = H^{(1)}_{\rm intl}(\xi^{(1)}_{\rm intl}) + H^{(2)}_{\rm intl}(\xi^{(2)}_{\rm intl}), \tag{2}$$

with eigenvalues $E_{\mathrm{intl},i} = E^{(1)}_{\mathrm{intl},i} + E^{(2)}_{\mathrm{intl},i}$, where $E^{(1)}_{\mathrm{intl},i}$ and $E^{(2)}_{\mathrm{intl},i}$ are energies of the separated monomers 1 and 2. The individual terms can vary enormously in complexity: each one may represent a structureless atom, requiring no internal Hamiltonian at all, a vibrating and/or rotating molecule, or a particle with electron and/or nuclear spins. The problems that arise in ultracold physics frequently involve pairs of atoms or molecules with electron and nuclear spins, often in the presence of external electric, magnetic or photon fields. All these complications can be taken into account in the structure of H_{intl} and the interaction potential $V(R, \xi_{\mathrm{intl}})$, which may both involve terms dependent on spins and external fields.

It is possible to solve the bound-state problem for the Hamiltonian (1) using basis sets for both the internal coordinates ξ_{intl} and the interparticle distance R. Such methods have been used with considerable success for highly excited states of molecules such as H_3^+ and H_2O on a single surface, often using discrete variable representations [10]. However, they have the disadvantage that the computer time generally scales as the cube of the number of radial basis functions. This problem becomes worse for levels very close to dissociation. It can be ameliorated to some extent by using sparse-matrix techniques and basis-set contraction, but the scaling remains poor.

An alternative is the *coupled-channel* approach, which handles the radial coordinate R by direct numerical propagation on a grid, and all the other coordinates using a basis set [11]. This is the approach that is implemented in BOUND and FIELD. It has the advantage that the computer time scales *linearly* with the number of points on the radial propagation grid. In the coupled-channel approach, the total wavefunction is expanded

$$\Psi(R, \xi_{\mathrm{intl}}) = R^{-1} \sum_j \Phi_j(\xi_{\mathrm{intl}}) \psi_j(R), \tag{3}$$

where the functions $\Phi_j(\xi_{\mathrm{intl}})$ form a complete orthonormal basis set for motion in the coordinates ξ_{intl} and the factor R^{-1} serves to simplify the form of the radial kinetic energy operator. The wavefunction in each *channel* j is described by a radial *channel function* $\psi_j(R)$. The expansion (3) is substituted into the total Schrödinger equation, and the result is projected onto a basis function $\Phi_i(\xi_{\mathrm{intl}})$. The resulting coupled differential equations for the channel functions $\psi_i(R)$ are

$$\frac{d^2\psi_i}{dR^2} = \sum_j \left[W_{ij}(R) - \mathcal{E}\delta_{ij} \right] \psi_j(R). \tag{4}$$

Here δ_{ij} is the Kronecker delta and $\mathcal{E} = 2\mu E/\hbar^2$, where E is the total energy, and

$$W_{ij}(R) = \frac{2\mu}{\hbar^2} \int \Phi_i^*(\xi_{\mathrm{intl}}) [\hbar^2 \hat{L}^2/2\mu R^2 + H_{\mathrm{intl}} + V(R, \xi_{\mathrm{intl}})] \Phi_j(\xi_{\mathrm{intl}}) \, d\xi_{\mathrm{intl}}. \tag{5}$$

The different equations are coupled by the off-diagonal terms $W_{ij}(R)$ with $i \neq j$.

The coupled equations may be expressed in matrix notation,

$$\frac{d^2\boldsymbol{\psi}}{dR^2} = \left[\mathbf{W}(R) - \mathcal{E}\mathbf{I} \right] \boldsymbol{\psi}(R). \tag{6}$$

If there are N basis functions included in the expansion (3), $\boldsymbol{\psi}(R)$ is a column vector of order N with elements $\psi_j(R)$, $\mathbf{I}$ is the $N \times N$ unit matrix, and $\mathbf{W}(R)$ is an $N \times N$ interaction matrix with elements $W_{ij}(R)$.

In general there are N linearly independent solution vectors $\boldsymbol{\psi}(R)$ that satisfy the Schrödinger equation subject to the boundary condition that $\boldsymbol{\psi}(R) \to 0$ at one end of the range. These N column vectors form a wavefunction matrix $\boldsymbol{\Psi}(R)$. The propagators in BOUND and FIELD all propagate the log-derivative matrix $\mathbf{Y}(R) = \boldsymbol{\Psi}'(R)[\boldsymbol{\Psi}(R)]^{-1}$, rather than $\boldsymbol{\Psi}(R)$ itself.

The particular choice of the basis functions $\Phi_j(\xi_{\mathrm{intl}})$ and the resulting form of the interaction matrix elements $W_{ij}(R)$ depend on the physical problem being considered. The complete set of coupled equations often factorises into blocks determined by the symmetry of the system. In the absence of external fields, the *total angular momentum* J_{tot} and the *total parity* are conserved quantities. Different or additional symmetries arise in different physical situations. The programs are designed to loop over total angular

momentum and parity, constructing a separate set of coupled equations for each combination and solving them by propagation. These loops may be repurposed for other symmetries when appropriate.

BOUND and FIELD can also handle interactions that occur in external fields, where the total angular momentum is no longer a good quantum number.

1.1. Location of bound states

True bound states exist only at energies where all asymptotic channels are energetically closed, $E < E_{\mathrm{intl},i}$ for all i. Under these circumstances the bound-state wavefunction $\boldsymbol{\psi}(R)$ is a column vector of order N that must approach zero in the classically forbidden regions at both short range, $R \to 0$, and long range, $R \to \infty$.

Continuously differentiable solutions of the coupled equations that satisfy the boundary conditions at both ends exist only at specific energies E_n. These are the eigenvalues of the total Hamiltonian (1); we refer to them (somewhat loosely) as the eigenvalues of the coupled equations, to distinguish them from eigenvalues of other operators that also enter the discussion below.

Wavefunction matrices $\boldsymbol{\Psi}(R)$ that satisfy the boundary conditions in *one* of the classically forbidden regions exist at any energy. We designate these $\boldsymbol{\Psi}^+(R)$ for the solution propagated outwards from short range and $\boldsymbol{\Psi}^-(R)$ for the solution propagated inwards from long range. The corresponding log-derivative matrices are $\mathbf{Y}^+(R)$ and $\mathbf{Y}^-(R)$.

It is convenient to choose a matching distance R_{match} where the outwards and inwards solutions are compared. A solution vector that is continuous at R_{match} must satisfy

$$\boldsymbol{\psi}(R_{\mathrm{match}}) = \boldsymbol{\psi}^+(R_{\mathrm{match}}) = \boldsymbol{\psi}^-(R_{\mathrm{match}}). \tag{7}$$

Since the derivatives of the outwards and inwards solutions must match too, we also require that

$$\frac{d}{dR}\boldsymbol{\psi}^+(R_{\mathrm{match}}) = \frac{d}{dR}\boldsymbol{\psi}^-(R_{\mathrm{match}}) \tag{8}$$

so that

$$\mathbf{Y}^+(R_{\mathrm{match}})\boldsymbol{\psi}(R_{\mathrm{match}}) = \mathbf{Y}^-(R_{\mathrm{match}})\boldsymbol{\psi}(R_{\mathrm{match}}). \tag{9}$$

Equivalently,

$$\left[\mathbf{Y}^+(R_{\mathrm{match}}) - \mathbf{Y}^-(R_{\mathrm{match}})\right]\boldsymbol{\psi}(R_{\mathrm{match}}) = 0, \tag{10}$$

so that the wavefunction vector $\boldsymbol{\psi}(R_{\mathrm{match}})$ is an eigenvector of the log-derivative matching matrix, $\Delta\mathbf{Y} = [\mathbf{Y}^+(R_{\mathrm{match}}) - \mathbf{Y}^-(R_{\mathrm{match}})]$, with eigenvalue zero [11].

For each J_{tot} and symmetry block, BOUND propagates log-derivative matrices to a matching point R_{match}, both outwards from the classically forbidden region at short range (or from $R = 0$) and inwards from the classically forbidden region at long range. At each energy E, it calculates the multichannel node count [12], defined as the number of zeros of $\boldsymbol{\psi}(R)$ between R_{min} and R_{max}. Johnson [12] showed that this is equal to the number of eigenvalues of the coupled equations that lie below E. It may be calculated as a simple byproduct of the propagations and the matching matrix. BOUND uses the node count to determine the number of eigenvalues of the coupled equations in the specified range, and then uses bisection to identify energy windows that contain exactly one eigenvalue. In each such window, it uses a combination of bisection and the Van Wijngaarden-Dekker-Brent algorithm [13] to converge on the energy where an eigenvalue of the log-derivative matching matrix $\Delta\mathbf{Y}$ is zero. This energy is an eigenvalue of the coupled equations. The program extracts the local wavefunction vector $\boldsymbol{\psi}(R_{\mathrm{match}})$, and optionally calculates the complete bound-state wavefunction $\boldsymbol{\psi}(R)$ using the method of Thornley and Hutson [14].

FIELD operates in a very similar manner to locate eigenvalues of the coupled equations as a function of external field at fixed energy (or energy fixed with respect to a field-dependent threshold energy). The one significant difference is that the multichannel node count is not guaranteed to be a monotonic function of field, and it is in principle possible to miss pairs of states that cross the chosen energy in opposite directions as a function of field. In practice this seldom happens.

The choice of R_{match} is significant. It does not affect the energies or fields at which the matching condition (10) is satisfied, but it does affect the matching matrix at other energies or fields and hence the rate of convergence on eigenvalues of the coupled equations. In particular, it is usually inappropriate to place R_{match} far into a classically forbidden region.

1.2. Matrix of the interaction potential

In order to streamline the calculation of matrix elements for the propagation, BOUND and FIELD express the interaction potential in an expansion over the internal coordinates,

$$V(R, \xi_{\rm intl}) = \sum_{\Lambda} v_{\Lambda}(R) \mathcal{V}^{\Lambda}(\xi_{\rm intl}). \tag{11}$$

The specific form of the expansion depends on the nature of the interacting particles. The radial potential coefficients $v_{\Lambda}(R)$ may either be supplied explicitly, or generated internally by numerically integrating over $\xi_{\rm intl}$. The R-independent coupling matrices $\boldsymbol{\mathcal{V}}^{\Lambda}$ with elements $\mathcal{V}^{\Lambda}_{ij} = \langle \Phi_i | \mathcal{V}^{\Lambda} | \Phi_j \rangle_{\rm intl}$ are calculated once and stored for use in evaluating $W_{ij}(R)$ throughout the course of a propagation.

1.3. Matrices of the internal and centrifugal Hamiltonians

Coupled-channel theory is most commonly formulated in a basis set where $\hat{L}^2$ and $H_{\rm intl}$ are both diagonal. All the built-in coupling cases use basis sets of this type. The matrix of $H_{\rm intl}$ is $\langle \Phi_i | H_{\rm intl} | \Phi_j \rangle_{\rm intl} = E_{{\rm intl},i} \delta_{ij}$. The diagonal matrix elements of $\hat{L}^2$ are often of the form $L_i(L_i+1)$, where the integer quantum number L_i (sometimes called the partial-wave quantum number) represents the end-over-end angular momentum of the two particles about one another.

However, the programs also allow the use of basis sets where one or both of $\hat{L}^2$ and $H_{\rm intl}$ are non-diagonal. If $H_{\rm intl}$ is non-diagonal, it is expanded as a sum of terms

$$H_{\rm intl}(\xi_{\rm intl}) = \sum_{\Omega} h_{\Omega} \mathcal{H}^{\Omega}_{\rm intl}(\xi_{\rm intl}), \tag{12}$$

where the h_{Ω} are scalar quantities, some of which may represent external fields if desired. The programs generate additional coupling matrices $\boldsymbol{\mathcal{H}}^{\Omega}$ with elements $\mathcal{H}^{\Omega}_{ij} = \langle \Phi_i | \mathcal{H}^{\Omega}_{\rm intl} | \Phi_j \rangle_{\rm intl}$. These are also calculated once and stored for use in evaluating $W_{ij}(R)$ throughout the course of a propagation. A similar mechanism is used for basis sets where $\hat{L}^2$ is non-diagonal, with

$$\hat{L}^2 = \sum_{\Upsilon} \mathcal{L}^{\Upsilon}. \tag{13}$$

If $H_{\rm intl}$ is non-diagonal, the allowed energies $E_{{\rm intl},i}$ of the pair of monomers at infinite separation are the eigenvalues of $H_{\rm intl}$. The wavefunctions of the separated pair are represented by simultaneous eigenvectors of $H_{\rm intl}$ and $\hat{L}^2$.

1.4. Boundary conditions

For deeply bound states, it is often sufficient to require that $\boldsymbol{\Psi}(R) \to 0$ in the classically forbidden regions at short and long range, or equivalently that $\mathbf{Y}(R) \to \pm\infty$. However, there are circumstances where more general boundary conditions are required:

- In systems where $R = 0$ is energetically accessible, some states require $\mathbf{Y}(0) = 0$.
- In model systems with a Fermi pseudopotential, corresponding to a δ-function at the origin or elsewhere, a finite value of $\mathbf{Y}$ may be required.
- For states very close to dissociation, the wavefunction $\boldsymbol{\psi}(R)$ dies off very slowly at long range, and it may be inefficient to propagate far enough that $\boldsymbol{\psi}(R) \to 0$. For a single channel, the wavefunction approximately follows the Wentzel-Kramers-Brillouin (WKB) approximation in the far classically forbidden region,

$$\psi(R) = [k(R)]^{-\frac{1}{2}} \exp\left(\pm \int_{R_{\rm turn}}^{R} k(R')\, dR' \right), \tag{14}$$

$$\psi'(R) = [k(R)]^{-\frac{1}{2}} \left[\pm k(R) - \frac{1}{2} \frac{k'(R)}{k(R)} \right] \exp\left(\pm \int_{R_{\rm turn}}^{R} k(R')\, dR' \right), \tag{15}$$

$$Y(R) = \pm k(R) - \frac{1}{2} \frac{k'(R)}{k(R)}, \tag{16}$$

where $k(R) = [2\mu(V(R)-E)/\hbar^2]^{1/2}$ and $V(R)$ is an effective potential energy for the channel concerned. The + sign applies inside the inner turning point (where the phase integral itself is negative) and the − sign applies outside the outer turning point. The first term in Eq. 16 dominates either when $k(R)$ is large (in a strongly classically forbidden region) or when the interaction potential is nearly constant (at very long range). The term involving $k'(R)$ is therefore neglected in the implementation of WKB boundary conditions.

BOUND and FIELD allow the imposition of separate boundary conditions for $\mathbf{Y}$ in closed and in open channels at R_{min} and at R_{max}, and by default apply WKB boundary conditions for closed channels (neglecting the term involving $k'(R)$ in Eq. 16). This gives faster convergence with respect to R_{min} and R_{max} than $\mathbf{Y}(R) \to \pm\infty$.

1.5. Perturbation calculations

BOUND can calculate expectation values using a finite-difference approach [15]. After a bound state is located at energy $E_n^{(0)}$, BOUND repeats the calculation with a small perturbation $a\hat{A}(R)$ added to the Hamiltonian to obtain a modified energy $E_n(a)$. From perturbation theory,

$$E_n(a) = E_n^{(0)} + a\langle\hat{A}\rangle_n + \mathcal{O}(a^2), \tag{17}$$

where $\mathcal{O}(a^2)$ are second-order terms. The finite-difference approximation to the expectation value $\langle\hat{A}\rangle_n$ is

$$\langle\hat{A}\rangle_n = \frac{E_n(a) - E_n^{(0)}}{a}, \tag{18}$$

and is accurate to order a.

For built-in coupling cases, BOUND can calculate expectation values of an operator $\hat{A}$ that is made up of a product of one of the angular functions in the potential expansion and a power of R. For coupling cases implemented in plug-in basis-set suites, any required operator can be implemented in the basis-set suite.

1.6. Richardson extrapolation

For propagators that use equally spaced steps, the error in bound-state energies due to a finite step size is proportional to a power of the step size (in the limit of small steps). BOUND can obtain an improved estimate of the bound-state energy by performing calculations with two different step sizes and extrapolating to zero step size.

1.7. Reference energies

By default, the zero of energy used for total energies is the one used for monomer energies, or defined by the monomer Hamiltonians programmed in a plug-in basis-set suite. However, it is sometimes desirable to use a different zero of energy (reference energy). This may be specified:

- as a value given directly in the input file;
- as the energy of a particular scattering threshold or pair of monomer states, which may depend on external fields.

1.8. Locating zero-energy Feshbach resonances

Zero-energy Feshbach resonances occur at fields where bound states cross a scattering threshold as a function of external field, provided there is coupling between the bound state and the threshold. FIELD may be used to locate such crossings by choosing the energy of the desired threshold as the reference energy and setting the relative energy to zero.

1.9. Wavefunctions

The programs always extract the local wavefunction vector $\boldsymbol{\psi}(R_{\mathrm{match}})$ at the matching point. If desired, they can calculate the complete bound-state wavefunction $\boldsymbol{\psi}(R)$ using the method of Thornley and Hutson [14].

2. Systems handled

The programs provide built-in Hamiltonians and basis sets to handle a number of common cases. In particular, they can calculate bound states in the close-coupling approximation (with no dynamical approximations except basis-set truncation) for the following pairs of species:

1. Atom + linear rigid rotor [16];
2. Atom + vibrating diatom with interaction potentials independent of diatom rotational state [17];
3. Linear rigid rotor + linear rigid rotor [18, 19, 20];
4. Asymmetric top + linear molecule [21]
5. Atom + symmetric top (also handles near-symmetric tops and linear molecules with vibrational angular momentum) [22, 23];
6. Atom + asymmetric top [22] (also handles spherical tops [24]);
7. Atom + vibrating diatom with interaction potentials dependent on diatom rotational state [25];
8. Atom + rigid corrugated surface [26, 27] (band structure). At present, the code is restricted to centrosymmetric lattices, for which the potential matrices are real, and is not included in FIELD.

The close-coupling calculations are all implemented in a fully coupled space-fixed representation, with the calculations performed separately for each total angular momentum and parity.

In addition, the programs implement a variety of dynamical approximations (decoupling methods) that offer considerable savings of computer time at the expense of accuracy. Some of these are of significance only for scattering calculations, such as the effective potential approximation [28], the L-labelled coupled-states (CS) approximation [29] and the decoupled L-dominant approximation [30, 31]. However, bound-state calculations frequently use the helicity decoupling approximation [8], which is implemented in BOUND and FIELD in the framework of the CS approximation.

In addition to the built-in cases, the programs provide an interface that allows users to specify Hamiltonians and basis sets for different pairs of species. These have been used for numerous different cases, and routines are provided for two cases of current interest:

1. Structureless atom + $^3\Sigma$ molecule in a magnetic field, demonstrated for Mg + NH;
2. Two alkali-metal atoms in ^{2}S states, including hyperfine coupling, in a magnetic field, demonstrated for $^{85}Rb_2$.

3. Propagators

BOUND and FIELD can solve the coupled equations using a variety of different propagation methods, all of which propagate the log-derivative matrix $\mathbf{Y}(R)$ rather than the wavefunction matrix $\mathbf{\Psi}(R)$. Log-derivative propagators are particularly suitable for the bound-state problem, both because they allow a very simple form of the matching equation and because they inherently avoid the instability associated with propagating in the presence of deeply closed channels. The propagators currently implemented in BOUND and FIELD are:

- Log-derivative propagator of Johnson (LDJ) [32, 33]: This is a very stable propagator. It has largely been superseded by the LDMD propagator, but can be useful in occasional cases where that propagator has trouble evaluating node counts.

- Diabatic log-derivative propagator of Manolopoulos (LDMD) [34]: This is a very efficient and stable propagator, especially at short and medium range.

- Quasiadiabatic log-derivative propagator of Manolopoulos (LDMA) [35, 11]: This is similar to the LDMD propagator, but operates in a quasiadiabatic basis. It offers better accuracy than LDMD for very strongly coupled problems, but is relatively expensive. It is recommended for production runs only for very strongly coupled problems. However, it is also useful when setting up a new system, because it can output eigenvalues of the interaction matrix at specific distances (adiabats) and nonadiabatic couplings between the adiabatic states.

- Symplectic log-derivative propagators of Manolopoulos and Gray (LDMG) [36]: This offers a choice of 4th-order or 5th-order symplectic propagators. These are 1.5 to 3 times more expensive per step than the LDMD and LDJ propagators, but can have smaller errors for a given step size. They can be the most efficient choice when high precision is required.

- Airy propagator: This is the AIRY log-derivative propagator of Alexander [37] as reformulated by Alexander and Manolopoulos [38]. It uses a quasiadiabatic basis with a linear reference potential (which results in Airy functions as reference solutions). This allows the step size to increase rapidly with separation, so that this propagator is particularly efficient at long range.

Calculations with BOUND and FIELD may use different log-derivative propagators at short and long range. This is particularly useful for bound states close to a dissociation threshold, where it may be necessary to propagate inwards from very large values of R to obtain converged results. The AIRY propagator incorporates a variable step size, and can be used to propagate inwards with an initially very large but decreasing step size at very low cost. However, it is not particularly efficient when the interaction potential is fast-varying, so it is often used in combination with a fixed-step-size method such as the LDMD propagator at short and intermediate range.

4. Computer time

The computer time required to solve a set of N coupled equations is approximately proportional to N^3. The practical limit on N is from a few hundred to several thousand, depending on the speed of the computer and the amount of memory available.

The computer time also depends linearly on the number of radial steps required to solve the coupled equations to the desired accuracy. The step size required is typically proportional to the minimum local wavelength, so that the time scales approximately with $(\mu E_{\rm max}^{\rm kin})^{1/2}$, where $E_{\rm max}^{\rm kin}$ is the maximum local kinetic energy; for bound states near dissociation, $E_{\rm max}^{\rm kin}$ may be approximated by the well depth of the interaction potential.

5. Plug-in functionality

5.1. Potential or potential expansion coefficients

The programs internally express the interaction potential as an expansion over the internal coordinates, as in Eq. (11). The expansion coefficients $v_\Lambda(R)$ may be supplied in a variety of ways:

- For very simple potentials, where the functions $v_\Lambda(R)$ are sums of exponentials and inverse powers, the parameters that specify them may be supplied in the input file.
- For more complicated functions, plug-in routines may be supplied to return individual values of $v_\Lambda(R)$ at a value of R specified in the calling sequence.
- For most of the built-in coupling cases, plug-in routines may be supplied to return the unexpanded potential $V(R, \xi_{\rm intl})$ at specified values of R and the internal coordinates $\xi_{\rm intl}$. The general-purpose potential routine supplied then performs numerical quadrature over $\xi_{\rm intl}$ to evaluate the expansion coefficients $v_\Lambda(R)$ internally.
- If none of these approaches is convenient (or efficient enough), a replacement potential routine may be supplied to return the complete potential expansion at once (all values of $v_\Lambda(R)$ at a value of R specified in the calling sequence).

5.2. Basis sets and coupling matrices

The programs provide an interface for users to supply a set of routines that specify an additional type of basis set, select the elements that will be used in a particular calculation, and calculate the matrices of coupling coefficients for the operators $\mathcal{V}^\Lambda(\xi_{\rm intl})$ used to expand the interaction potential. The routines must also specify the matrices of $H_{\rm intl}$ and $\hat{L}^2$, which may be diagonal or non-diagonal. If desired, $H_{\rm intl}$ may contain terms that depend on external fields.

5.3. External fields and potential scaling

The programs incorporate data structures to handle external electric, magnetic or photon fields. There may be multiple fields at arbitrary relative orientations. Internally, the field-dependent terms in the Hamiltonian are a subset of those in $H_{\rm intl}$,

$$H_{\rm intl}(\xi_{\rm intl}, \boldsymbol{B}) = \sum_{\Omega} B_{\Omega} \mathcal{H}^{\Omega}_{\rm intl}(\xi_{\rm intl}), \tag{19}$$

where the vector $\boldsymbol{B}$ represents all the fields present. The elements of $\boldsymbol{B}$ may each be expressed as a *nonlinear* function of external field variables (EFVs); the EFVs may thus (for example) represent the magnitudes, orientations, or relative angles of the component fields. BOUND allows calculations on a grid of values of any one EFV, and FIELD allows bound states to be located as a function of one EFV with all the others fixed.

The programs also allow calculations as a function of a scaling factor that multiplies the entire interaction potential, or a subset of the potential expansion coefficients $v_\Lambda(R)$. The scaling factor is handled internally using the same structures as external fields.

6. Distributed files and example calculations

6.1. Distributed files

The program is supplied as a tarred zipped file, which contains:

- the full program documentation in pdf format;
- a directory `source_code` containing
  - the Fortran source code;
  - a GNU makefile (`GNUmakefile`) that can build the executables needed for the example calculations;
- a directory `examples` containing
  - a sub-directory `input` containing input files for the example calculations described below;
  - a sub-directory `output` containing the corresponding output files;
- a directory `data` containing auxiliary data files for some potential routines used in the example calculations;
- a plain-text file `README` that gives information on changes that may be needed to adapt the GNUmakefile to a specific target computer.
- a plain-text file `COPYING` that contains the text of the GNU General Public License, Version 3.

6.2. Example calculations

The executables used for different calculations may differ in the routines linked to construct the basis set, specify the internal Hamiltonian, and evaluate the interaction potential. The executables required for the example calculations can all be built using `GNUmakefile`.

6.2.1. All available propagators

input file: `bound-all_propagators.input`
executable: `bound-basic`

`bound-all_propagators.input` performs close-coupling calculations on the bound states of a simple model of a complex formed between an atom and a linear rigid rotor. The radial potential coefficients are provided in the input data file and consist of a Lennard-Jones 12-6 potential for $\lambda = 0$ and a dispersion-like R^{-6} form for $\lambda = 2$. The calculation is repeated using combinations of short-range and long-range propagators that exercise every propagation method available in BOUND (though not every possible combination). The calculation is done twice for the LDMD/AIRY combination; once with $R_{\mathrm{mid}} < R_{\mathrm{match}}$ and once with $R_{\mathrm{mid}} > R_{\mathrm{match}}$. The calculation which uses just the LDMD propagator employs a different step length for the inwards propagation. This input file should produce the same results regardless of which BOUND executable is used.

6.2.2. Bound states of Ar-HCl with expectation values

input file: `bound-Ar_HCl.input`
executable: `bound-Rg_HX`

`bound-Ar_HCl.input` performs calculations on the states of Ar-HCl bound by more than 80 cm^{-1}, using the H6(4,3,0) potential of Hutson [39] and the LDMD propagator, for total angular momentum $J_{\mathrm{tot}} = 0$ and 1 and both parities. The first run does close-coupling calculations. The second run does calculations in the helicity decoupling approximation, and in addition calculates expectation values $\langle P_2(\cos\theta)\rangle$ and $\langle 1/R^2\rangle$ for all the states. The results may be compared with Table IV of ref. [39]. The third run calculates the wavefunction for the first bound state identified in the first run. The wavefunction is written to unit 109; the resulting file is included as `bound-Ar_HCl.wavefunction` in `examples/output`. The components may be plotted with any standard plotting package.

6.2.3. Bound states of Ar-CO_2 with Richardson extrapolation

input file: `bound-Ar_CO2.input`
executable: `bound-Rg_CO2`

`bound-Ar_CO2.input` performs close-coupling calculations on the ground and first vibrationally excited state of Ar-CO_2, using the split repulsion potential of Hutson *et al.* [40] and the LDJ propagator, for total angular momentum $J_{\mathrm{tot}} = 0$. The results may be compared with Table IV of ref. [40].

It first calculates the ground-state energy using a fairly large (unconverged) step size of 0.03 Å. It then repeats the calculation with an even larger step size, and extrapolates to zero step size using Richardson h^4 extrapolation.

6.2.4. Bound states of Ar-H_2

input file: `bound-Ar_H2.input`
executable: `bound-Rg_H2`
also required: `data/h2even.dat`

`bound-Ar_H2.input` performs close-coupling calculations on the ground state of Ar-H_2 with H_2 in its $v = 1$, $j = 1$ state, for total angular momentum $J_{\mathrm{tot}} = 1$ and even parity ($j + L$ even). For this parity there is no allowed $j = 0$ channel, so the state is bound except for vibrational predissociation to form H_2 ($v = 0$) [41], which is not taken into account by BOUND. The run uses the LDMD propagator and the TT3(6,8) potential of Le Roy and Hutson [42], evaluated for H_2 states $(j, v) = (0, 0)$, (2,0) and (4,0) using H_2 matrix elements provided in the file `data/h2even.dat`.

BOUND first calculates the ground-state energy using a fairly large (unconverged) step size of 0.04 Å. It then repeats the calculation with an even larger step size, and extrapolates to zero step size using Richardson h^4 extrapolation.

6.2.5. Bound states of H_2-H_2 (ortho-para)

input file: `bound-ityp3.input`
executable: `bound-H2_H2`

`bound-ityp3.input` performs close-coupling calculations on bound states of H_2-H_2 with one para-H_2 molecule (even j) and one ortho-H_2 molecule (odd j). It uses the LDMD propagator. The interaction potential is that of Zarur and Rabitz [43]. The states are bound by less than 2 cm^{-1} (below the $j = 0 + j = 1$ threshold).

6.2.6. Bound states of He-NH_3

input file: `bound-ityp5.input`
executable: `bound-basic`

`bound-ityp5.input` performs close-coupling calculations on bound states of He-NH_3, taking account of the tunnelling splitting of NH_3, using a simple analytical interaction potential and the LDMD propagator. The input file selects rotational functions of E symmetry by setting `ISYM(3)` to 1 and specifies that the H nuclei are fermions by setting `ISYM(4)` to 1.

6.2.7. Bound states of Ar-CH_4

input file: `bound-Ar_CH4.input`
executable: `bound-Ar_CH4`

`bound-Ar_CH4.input` performs close-coupling calculations on bound states of Ar-CH_4, using `ITYPE` = 6. It uses the interaction potential of Buck *et al.* [44]. It uses the LDMD propagator. CH_4 is a spherical top, and the input file selects rotor functions of F symmetry and even k by setting `ISYM` to 177. The results may be compared with Table II of ref. [24].

6.2.8. Bound-state energies of the hydrogen atom

input file: `bound-hydrogen.input`
executable: `bound-basic`

`bound-hydrogen.input` carries out single-channel bound-state calculations on the hydrogen atom, and demonstrates how to handle calculations in atomic units. It sets `MUNIT` to the electron mass in Daltons, `RUNIT` to the Bohr radius in Å and `EUNITS` = 7 to select input energies in hartrees. It sets up a simple Coulomb potential, with the energy scaling factor set to the hartree in cm^{-1}, so that the potential is handled in atomic units. It uses the atom-rigid rotor basis with `JMAX` = 0 to generate a simple single-channel problem. Note that `ROTI(1)` is set to the dummy value `1.0`; this value is not used because `JMAX` = 0, but it prevents the program terminating prematurely.

The wavefunction at the origin is of the form r^{l+1}, so its log-derivative is infinite at the origin. This is the default for locally closed channels, but is specified explicitly for the locally open $l = 0$ channel.

Because `JMAX` = 0, the orbital angular momentum l is equal to `JTOT`. `JTOT` = 0 produces ns levels at energies of $-1/(2n^2)$ for $n = 1, 2, ...$, while `JTOT` = 1 produces np levels starting at $n = 2$.

6.2.9. Bound-state energies of Mg + NH at specified magnetic fields

input file: `bound-Mg_NH.input`
executable: `bound-Mg_NH`
also required: `data/pot-Mg_NH.data`

`bound-Mg_NH.input` locates the bound states of MgNH at specified magnetic fields. It uses a plug-in basis-set suite for a $^3\Sigma$ diatom colliding with a structureless atom. Radial potential coefficients are obtained by RKHS interpolation of the potential points of Soldán *et al.* [45]. The coupled equations are solved using the LDMD/AIRY hybrid propagation scheme.

The run locates a single bound state at four different magnetic fields from 370 G to 385 G, from which it may inferred that the state will cross threshold near 387 G.

6.2.10. Bound states of Mg + NH as a function of magnetic field

input file: `field-Mg_NH.input`
executable: `field-Mg_NH`
also required: `data/pot-Mg_NH.data`

`field-Mg_NH.input` locates magnetic fields in the range 0 to 400 G at which bound states exist for specific energies relative to the lowest scattering threshold of Mg + NH in a magnetic field. It uses the same basis-set suite and interaction potential as in section 6.2.9. The coupled equations are solved using the LDMD/AIRY hybrid propagation scheme.

The run locates the same level as in section 6.2.9 at energies of 0, 20 and 40 MHz $\times$ h below threshold, and shows that it crosses threshold near 387.28 G.

6.2.11. Locating threshold crossings for $^{85}Rb_2$

input file: `field-basic_Rb2.input`
executable: `field-Rb2`

`field-basic_Rb2.input` locates magnetic fields where bound states cross the lowest scattering threshold for $^{85}Rb_2$. These are the fields at which zero-energy Feshbach resonances exist. It uses a plug-in basis-set suite for a pair of alkali-metal atoms in a magnetic field, including hyperfine interactions. It uses the potential of Strauss *et al.* [46], implemented with potential coefficients incorporated in the executable. The coupled equations are solved using the LDMD/AIRY hybrid propagation scheme.

The basis-set suite for this interaction requires information about the hyperfine properties of the atoms in an additional namelist block named `&BASIS9`. The potential expansion comprises 3 terms: the singlet and triplet interaction potentials, and the spin-spin dipolar term, which is modelled in the form

$$\lambda(R) = E_\mathrm{h}\alpha^2 \left[\frac{g_S^2}{4(R/a_0)^3} + A\exp(-\beta R/a_0)\right]. \tag{20}$$

6.2.12. Bound states of $^{85}Rb_2$ as a function of magnetic field

input file: `field-Rb2.input`
executable: `field-Rb2`

`field-Rb2.input` locates bound states of $^{85}Rb_2$ as a function of magnetic field, using the same potential and basis-set suite as in section 6.2.11. The calculation locates the magnetic fields (in the range 750 to 850 G) at which bound states exist with binding energies of 225, 175, 125, 75 and 25 MHz below the lowest threshold. There are, however, two bound states that these calculations fail to find, as they run almost parallel to the threshold, at about 140 and 220 MHz below it. To locate these bound states, one would need to do a calculation using BOUND.

7. Program history

BOUND was originally written by Jeremy Hutson in 1984 to calculate bound states of van der Waals complexes by coupled-channel methods, using the same structures as MOLSCAT [47] to generate the coupled equations. Subsequent versions incorporated basis-set enhancements as they were made in MOLSCAT. A fundamental change was made in BOUND version 5 (1993) to base the convergence algorithm on individual eigenvalues of the log-derivative matching matrix [11], rather than its determinant. Versions 4 (1992) and 5 (1993) [48] were distributed via CCP6, the Collaborative Computational Project on Heavy Particle Dynamics of the UK Science and Engineering Research Council.

BOUND was extended to handle calculations in external electric and magnetic fields in 2007. FIELD was written by Jeremy Hutson in 2010, using the same structures as BOUND to generate the coupled equations but designed to locate bound states as a function of external field at fixed energy, rather than as a function of energy.

There has been no fully documented publication of BOUND since version 5, and FIELD has never been published.

7.1. Principal changes in version 2019.0

- The basis-set plug-in mechanism has been extended to allow propagation in basis sets that are not eigenfunctions of the internal Hamiltonian H_intl. This makes implementing new types of system much simpler than before, especially where the individual interaction partners have complicated Hamiltonians.

- The basis-set plug-in functionality has been used to add new capabilities to carry out calculations in external fields (electric, magnetic, and/or photon) and to loop over (sets of) values of the fields.
- The distance at which the calculation switches between short-range and long-range propagators (R_{mid}) is now distinct from the distance at which the incoming and outgoing wavefunctions are matched (R_{match}).
- The programs now do an outwards propagation from R_{min} to R_{match} and an inwards propagation from R_{max} to R_{match}. The node count is calculated without needing a third propagation from R_{match} to R_{min} or R_{max}.
- A more general mechanism for combining propagators has been implemented, allowing any sensible combination of propagators at short and long range.
- A more general choice of log-derivative boundary conditions at the starting points for propagation is now allowed.
- An additional propagation approach [36] has been included, implemented by George McBane, which takes advantage of the symplectic nature of the multichannel radial Schrödinger equation.

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